A viscometric study of cement pastes containing superplasticizers with a note on experimental techniques

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A viscometric study of cement pastes containing superplasticizers with a note on experimental techniques

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SYNOPSIS

Viscometric data on the influence of concentration of two superplasticizing admixtures upon the yield value and plastic viscosity of pastes made with four cements are reported. Yield value decreases exponentially with concentration, whilst plastic viscosity decreases linearly. These results are discussed in relation to the effect of superplasticizers upon the rheology of fresh concrete. Detailed differences in results obtained in viscometers of different geometries are reported and discussed.

Introduction

Superplasticizing admixtures are widely used in the production of highly workable concrete, 'flowing concrete', without using excessively high water contents. A previous paper described a study of the effect of concentration of superplasticizing admixtures upon the yield value and plastic viscosity of concrete[1]. It is reasonable to assume that fresh concrete rheology is dependent, inter alia, upon cement paste rheology, but the exact nature of the relationship has not been established. Now that a convenient and precise apparatus for the determination of the flow properties of fresh concrete has been developed[2], it is possible to make meaningful comparisons between the rheology of concrete and its constituent cement paste. The aims of the work described in this paper were two-fold: (1) to discover whether any similarity exists between the effects of superplasticizing admixtures upon concrete and upon cement pastes, thereby contributing to our knowledge of the dependence of fresh concrete rheology upon cement paste rheology, and (2) to investigate the effect of superplasticizing admixtures upon cement paste rheology, thereby gaining an insight into the mechanism of their action.

In the previous study[1], all combinations of four cements and two admixtures, one sulphonated melamine formaldehyde and one sulphonated naphthalene formaldehyde condensate, were studied. It was found that yield value decreased approximately exponentially to a minimum value and that plastic viscosity probably increased to a maximum before decreasing again. The minimum yield value was reached at about 0·6–0·7% resin solids by weight of cement, which coincided with the peak in the plastic viscosity relationship. This finding agreed closely with the adsorption studies of Daimon and Roy[3], which showed that saturation appeared to be achieved at 0·66% of solids by weight of cement.

The approximately exponential decay of yield value of concrete is confirmed in Figure 1, where the data from reference 1 are plotted as the log of the relative yield value of concrete, expressed as the ratio of yield value to that at zero admixture concentration, against concentration. The least-squares regression

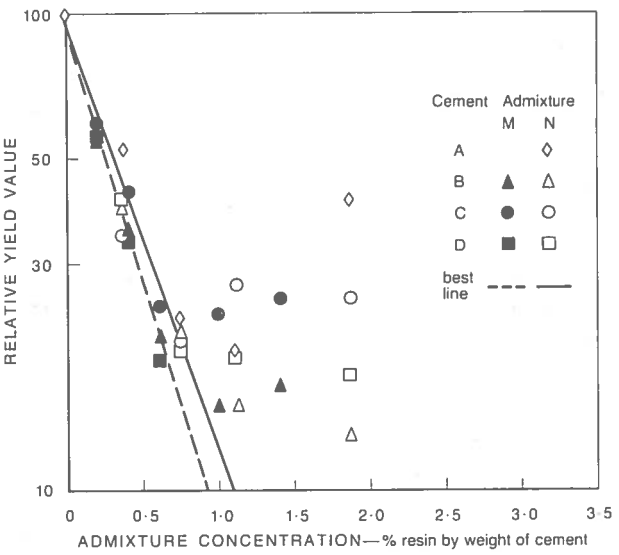


Figure 1: Variation of yield value of concrete with superplasticizer concentration.

lines for the two admixtures at concentrations below 1·0% are shown. The relationship is of the form

$$\ln \tau_y = D - kc \quad \ldots\ldots\ldots\ldots (1)$$

where c is the concentration and D a constant. The correlation coefficient is 0·988 and the slopes, k, of −2·1 and −2·5 are not significantly different. There is thus no difference in the effect of the two admixtures in concrete.

Rheology of cement pastes

The rheology of cement pastes has been studied over 30 years, but it cannot be said that a measure of agreement has been reached either qualitatively or quantitatively, although most workers report approximately Bingham plastic behaviour where

$$\tau = \tau_y + \mu_p \dot{\gamma} \quad \ldots\ldots\ldots\ldots (2)$$

in which τ is shear stress, γ shear rate, τ_y yield value and μ_p plastic viscosity. Of those who have studied flow curves[4–15] some have found what they term thixotropic behaviour, i.e. in an experiment where shear rate is increased and decreased cyclically, the down-curve falls to lower shear stresses than the up-curve. This is not thixotropy, because the structure does not re-form on standing and a subsequent cycle is generally at still lower shear stresses, indicating irreversible time-dependent structural breakdown. Other workers have found the reverse, i.e. structural build-up during the experiment. This could be caused by hydration during the course of the experiment. Because of the difficulty of analysing hysteresis loops, the other main body of research[16–21] has used continuous shear techniques at a constant shear rate. All of these workers have observed structural breakdown, but recent unpublished work by Banfill has shown that, if the experiment is continued after breakdown is complete, structural build-up occurs, presumably owing to hydration of the paste.

The most systematic study has been that of Tattersall and Dimond[20], who observed that, during the course of a breakdown experiment in coaxial cylinders, a stationary plug of material formed which produced discontinuities in the breakdown behaviour. In smooth cylinders, the plug either disintegrated or slid round at a lower velocity than that of the inner cylinder. With serrated cylinders, the plug was always stationary and its dimensions could be used to reconcile otherwise anomalous results by assuming that its only effect was to change the geometry of the system. They recommended that, in all future work on cement paste, serrated cylinders should be used and the paste critically examined for the existence of a plug.

In view of the above, it is not surprising that few workers have studied the effects of admixtures upon cement paste rheology. Wittmann[13] measured the change in viscosity with additions of a sulphonated melamine formaldehyde resin. However, he gives insufficient details of apparatus and procedure to enable us to decide whether the reported viscosity is the apparent viscosity (at an undefined shear rate) or the plastic viscosity. No information on changes in yield value is given. Addition of resin reduces the viscosity of cement pastes.

Petrie[22] measured the flow curves of cement pastes containing sodium alkylnaphthalene sulphonates with a Brookfield rotating-disc viscometer. He found that, as concentration increased, the flow behaviour progressively changed from Bingham, but with structural breakdown, towards reversible Newtonian, i.e. the width of the hysteresis loop decreased and the yield value decreased to zero at 1·5% resin/cement.

This was confirmed by Banfill[23] using coaxial cylinders with profiled (ribbed) surfaces. A content of 0·8% sulphonated naphthalene formaldehyde resin solids by weight of cement was sufficient to reduce the yield value and hysteresis loop area almost to zero.

Roy and Asaga[14, 15] studied the variation of yield value and apparent viscosity of cement pastes with the same type of admixture, using different preparation and mixing methods, different water/cement ratios and different concentrations. Their apparatus was similar to Banfill's, but had smaller ribbed cylinders. Discussion of their results is complicated by the fact that apparent viscosities are reported instead of plastic viscosities, in spite of the close approximation to Bingham behaviour. Careful scrutiny of their flow curves shows that increasingly vigorous mixing procedures reduced the yield value of plain pastes but had little effect upon plastic viscosity. This is consistent with the destruction of structure by mixing, but their flow curves all show structural build-up. This could be due to the long time taken to complete a flow curve – 15 minutes for an up-and-down cycle. During this time sufficient hydration might occur to manifest itself as structural build-up. Taking the yield value and the plastic viscosity from the approximately straight-line up-curves shows that addition of up to 0·45% admixture solids progressively decreased the yield value from about 50–60 N/m² at 0·35 and 0·40 water/cement ratio to zero. At w/c = 0·30, the yield value fell from 200 to 5 N/m². At w/c = 0·40, plastic viscosity was unaffected by admixture. At w/c = 0·35 and 0·30, plastic viscosity decreased sharply between 0·22 and 0·37% admixture, typical values being 0·1–0·3 N s/m².

They reported isolated results for a sulphonated melamine formaldehyde admixture, but these serve no use other than to indicate that the yield values and plastic viscosities were comparable. No other work on this type of admixture is known, but it is reasonable to expect similar behaviour, particularly in view of their similarity in concrete.

Experimental section

The materials used were as follows.

Cement. Four cements designated A, B, C and D were used. They are the same as were used in reference 1, and their physical and chemical properties are summarized in Appendix 1.

Admixtures. Two admixtures were used. These were a sulphonated melamine formaldehyde resin (type M), solids content 20%; and a sulphonated naphthalene formaldehyde resin (type N), solids content 37%.

Water. De-ionized water was used in all mixes.

The experimental procedure was standardized as follows: 250 g of cement was mixed by hand with 87·5 g of water containing the appropriate quantity of admixture (0·35 water/cement ratio), for 3 min in a crystallizing dish with a spatula. No special steps were taken to remove air from the mix. At the end of this time the paste was divided into three portions and the up and down flow curves determined in three viscometer geometries. The time to the start of each flow curve and the maximum speed and shear rate reached are shown in Table 1. The measurements were carried out by using a Haake Rotovisco RV2 viscometer with the MK 500 torque measuring head and the PG 142 external speed programmer. In all cases the complete up-and-down curve taking 2 min was recorded on an X–Y plotter.

The MV11P geometry is a pair of coaxial cylinders, bob radius 18·4 mm, cup radius 21 mm, bob height 60 mm. The surfaces are profiled with ribs 0·1 mm high by 0·1 mm wide running parallel to the axis, spaced 2 mm apart.

The S13/15 geometry, used by Tattersall and Dimond[20] is a pair of coaxial cylinders, bob radius 13 mm, cup radius 15 mm, bob height 50 mm. The surfaces have square-section serrations, 0·5 mm high by 0·5 mm wide.

The H/MVS geometry is a scaled-down version of the interrupted helical ribbon impeller used by Tattersall and Bloomer for the measurement of workability of concrete[2]. It is intended to obviate sedimentation during the experiment by imparting vertical as well as rotational motion. The impeller is shown in Figure 2, and rotates in a smooth cylinder of

TABLE 1: **Flow curve experimental conditions.**

Geometry	Time from mixing (min)	Maximum speed (rev/min)	Angular velocity (rad/s)	Maximum shear rate (s^{-1})
MV11P	5	200	20·9	176
S13/15	10	200	20·9	168
H/MVS	15	1000	104·7	188

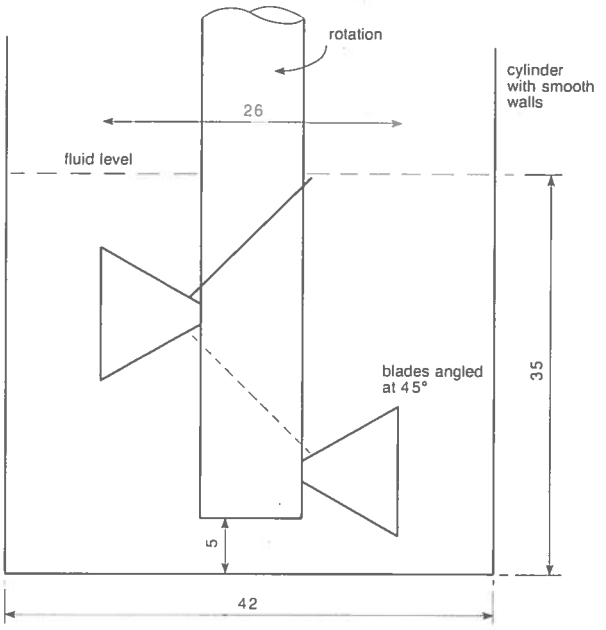


Figure 2: Helical impeller geometry for cement pastes.

21 mm radius. The value of shear rate given in Table 1 for this geometry is the mean shear rate determined from the theory of reference 2 for a series of Newtonian and pseudoplastic fluids. The shear rates for the other geometries are those at the inner cylinder obtained from conventional rotational viscometric equations.

Calculation of results from flow curves

Figure 3 shows typical flow curves obtained in the three geometries. The yield value τ_y and plastic viscosity μ_p are determined for coaxial cylinders geometries applying the Reiner–Riwlin equation[24] to the down-curve:

$$\Omega = \frac{\Gamma}{4\pi\mu_p}\left(\frac{1}{r_1^2} - \frac{1}{r_2^2}\right) - \frac{\tau_y}{\mu_p}\ln\left(\frac{r_1}{r_2}\right) \quad \ldots\ldots(3)$$

where Γ is the torque per unit height. The slope of the line gives the plastic viscosity. The intercept of the down-curve on the torque axis is related to the yield value:

$$\Gamma = 2\pi r_1 \tau_y \quad \ldots\ldots\ldots\ldots(4)$$

For the H/MVS geometry, the down-curve is a straight line over most of its length conforming to the equation

$$T = \alpha + \beta\Omega \quad \ldots\ldots\ldots\ldots(5)$$

where α and β are proportional to τ_y and μ_p respectively. The constants of proportionality determined by the theory of reference 2 give:

$$\tau_y = 32{\cdot}8\alpha \quad \text{N/m}^2$$
$$\mu_p = 18{\cdot}2\beta \quad \text{N s/m}^2$$

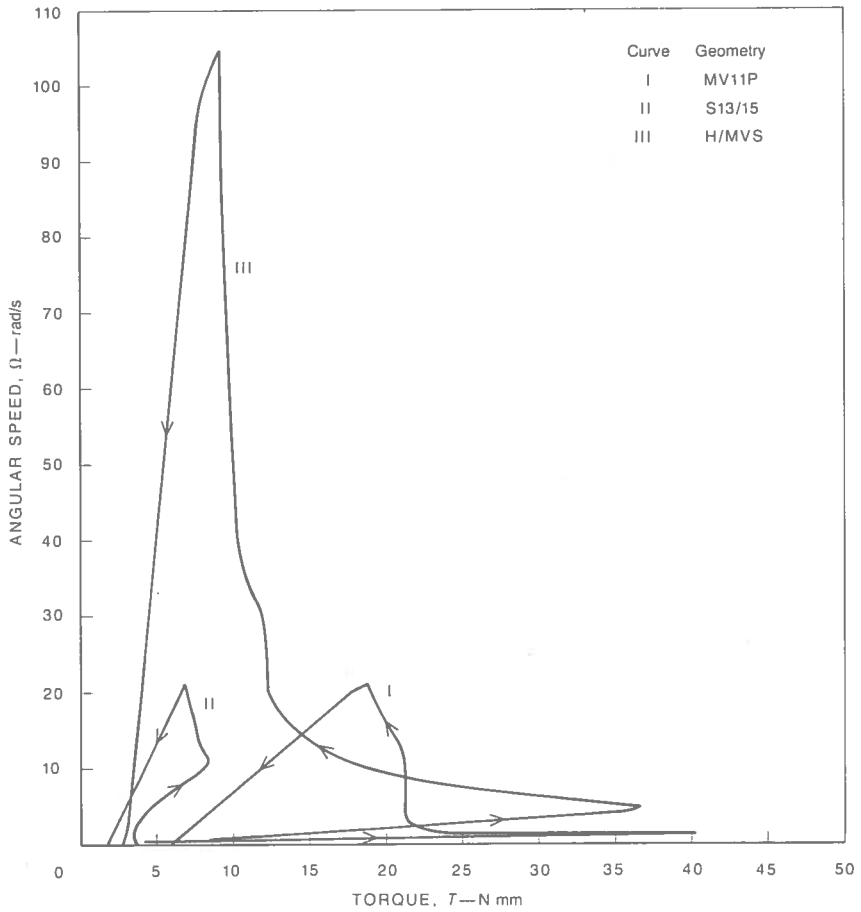


Figure 3: Typical flow curves for the three geometries.

The three down-curves shown in Figure 3 therefore give the yield values and plastic viscosities shown in Table 2.

Experimental programme

The main experimental programme was a study of pastes prepared as described above in the three geometries. Different concentrations of admixtures were used, up to 3% resin solids by weight of cement. Subsidiary investigations were carried out to account for discrepancies in some of the results, and these will be discussed in the appropriate place.

TABLE : **Data derived from the down-curves in Figure 3.**

Geometry	Yield value (N/m^2)	Plastic viscosity ($N\ s/m^2$)
MV11P	45	0·5
S13/15	30	0·6
H/MVS	95	0·9

Results

The yield value and plastic viscosity of three batches of paste made with each cement were determined for each geometry. The mean values are shown in Table 3, together with an estimate of the standard deviation obtained with each geometry, to show the experimental error. Differences between the geometries are discussed later. A consistent bias in the results is possible because the times from mixing to testing varied from 5 to 15 min. However, preliminary experiments showed that there was no significant difference in the results for any one geometry, whether tested after 5, 10 or 15 min, so this effect can be ignored in making comparisons.

Since the parameters for the paste vary from cement to cement when no admixture is present, the effect of admixture concentration is given relative to 0% admixture. Figures 4 and 5 show the variation of yield value and plastic viscosity with concentration of type M and type N admixture. No distinction is made between geometries or cements. The 90% confidence limits derived from Table 3 are shown in the Figures.

TABLE 3: **Rheological parameters for 0·35 w/c pastes of cements A to D.**

Geom-metry	Cement*								Over-all mean		Standard deviation	
	A		B		C		D					
	τ_y (N/m²)	μ_p (N s/m²)	τ_y (N/m²)	μ_p (N s/m²)	τ_y (N/m²)	μ_p (N s/m²)	τ_y (N/m²)	μ_p (N s/m²)	τ_y (N/m²)	μ_p (N s/m²)	τ_y (N/m²)	μ_p (N s/m²)
MV11P	60	0·8	35	0·5	30	0·5	35	0·5	40·2	0·56	5·8	0·07
S13/15	35	0·8	30	0·6	30	0·6	30	0·6	30·0	0·62	3·5	0·10
H/MVS	110	1·3	95	1·0	60	1·0	90	0·8	89·1	1·05	9·8	0·10

*Each entry is the mean of three pastes.

Discussion

EFFECTS OF CONCENTRATION

Figures 4 and 5 show that the broad trend of yield value with concentration found in the concrete experiments is repeated with cement pastes but the plastic viscosity decreases initially before increasing towards higher concentrations – the reverse behaviour to that found with concrete.

The linear regression lines of paste plastic viscosity against concentration are shown over the decreasing section. Despite the wide scatter of individual results, the correlation coefficients, 0·67 for type M and 0·44 for type N admixture, are significant at the 1% level. Additionally the slopes of the lines, −0·7 for type M and −0·2 for type N, are significantly different at the 5% level, so that plastic viscosity of cement pastes is more strongly affected

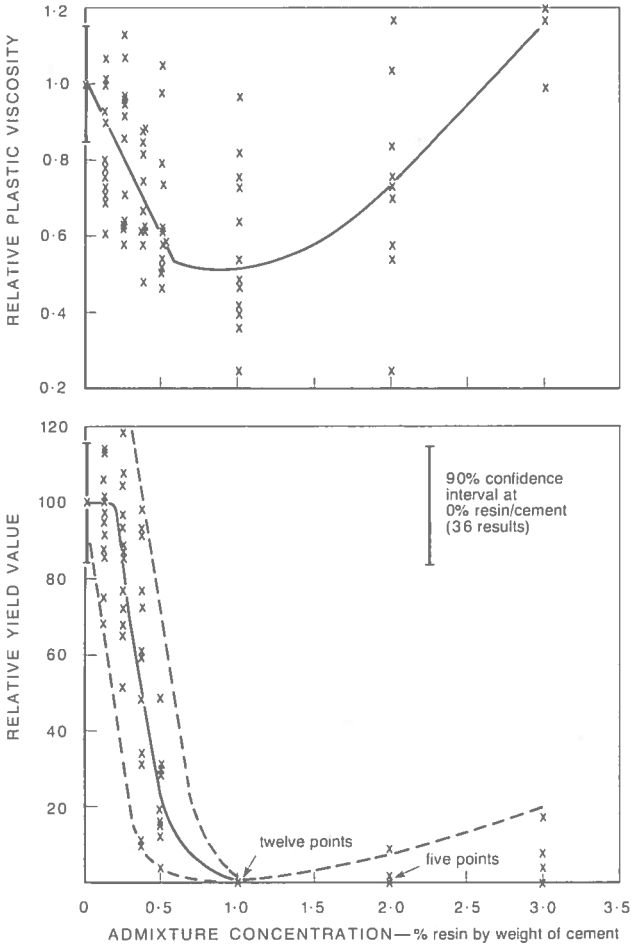


Figure 4: Effect of concentration of type M admixture upon yield value and plastic viscosity.

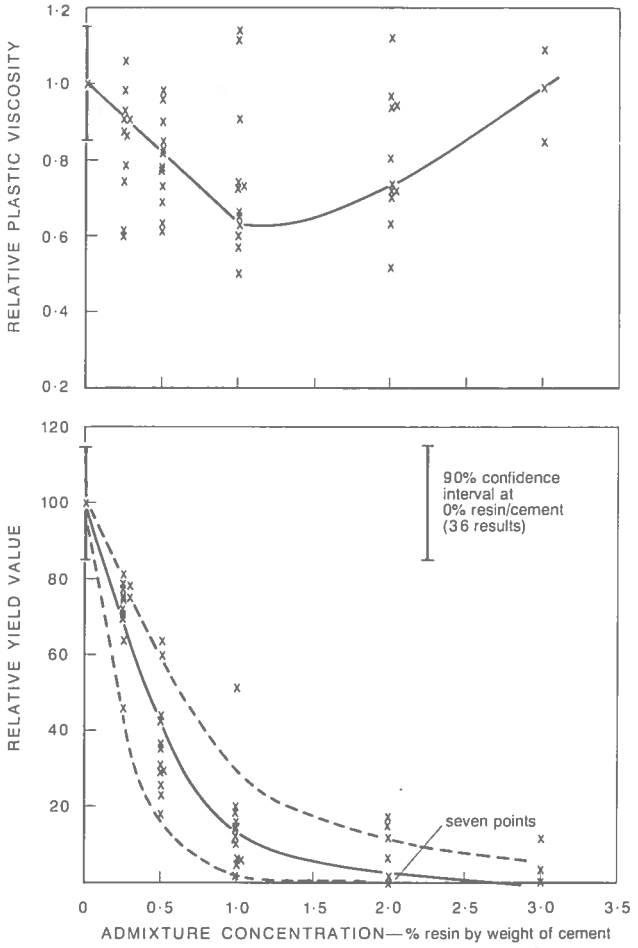
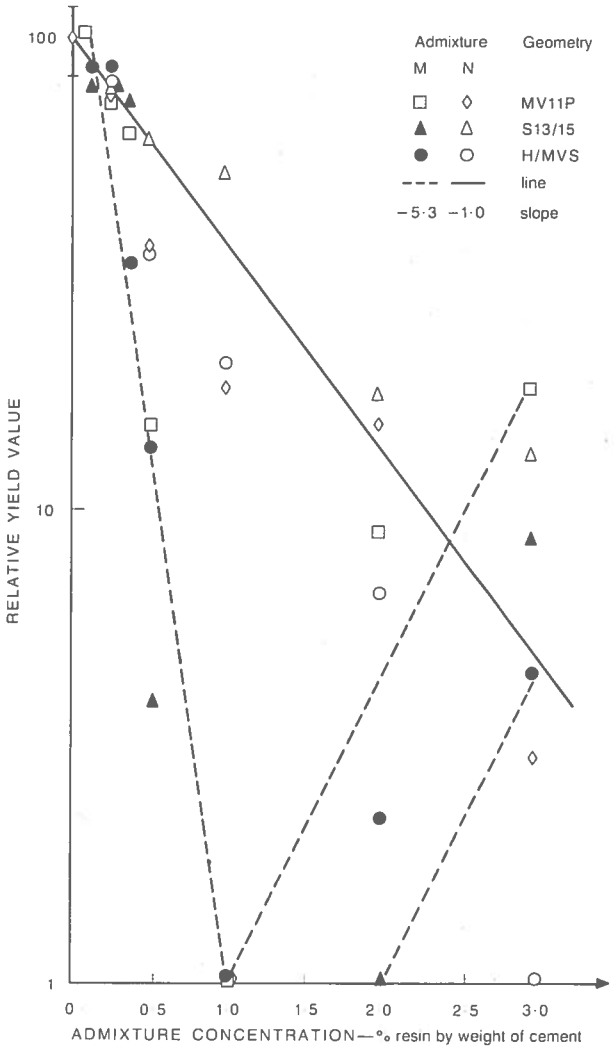


Figure 5: Effect of concentration of type N admixture upon yield value and plastic viscosity.

by type M than by type N admixture. Scrutiny of the individual results shows that there is no variation in the slope of the plot for different cements.

The correlation between paste yield value and concentration is also significant at the 1% level and agrees with the exponential relationship of equation 1, but differs in detail between cements and between admixtures. Since the concrete experiments were carried out at fixed mix proportions, the relationship of equation 1 is solely the effect of the admixture and this is evidence in favour of a direct relationship between the yield value of a concrete and the yield value of its constituent paste. This assumes that the effect of concentration upon paste yield value is the same at w/c = 0·35 as at w/c = 0·65. This is a reasonable assumption, but there is no experimental evidence for or against it. However, Figures 4 and 5 show that yield value of the paste decreases to a value experimentally indistinguishable from zero at high admixture concentrations, whilst Figure 1 shows that there is always a residual minimum yield value in concrete. Clearly part of the yield value in concrete is due to the presence of aggregate.

On the other hand, a causal relationship between plastic viscosity of concrete and its constituent paste is not identified, as addition of admixture changes their plastic viscosity in opposite directions. However, this might be accounted for by the following mechanism. Admixture disperses the agglomerates of cement particles in the paste, either by changing electrostatic interactions[3] or by steric effects[23]. This reduced attraction between particles reduces the resistance to flow of the paste, i.e. the plastic viscosity. But in concrete the larger aggregate particles must also pass each other and it can be argued that the role of the paste is in separating these particles. In undispersed paste this separation is achieved by large agglomerates of cement particles. When admixture is added, these agglomerats are dispersed, possibly into individual particles, and this allows aggregate particles to approach each other more closely. The distance of closest approach is reduced from the diameter of an agglomerate containing hundreds of particles to the diameter of a single cement particle. This increased contact between aggregate particles in concrete increases its plastic viscosity, even though the plastic viscosity of the paste decreases. This is consistent with the experimental observation that changing the aggregate particle size distribution changes the plastic viscosity of a concrete, and this argument suggests that the effect of particle size extends into the size range of cement particles. On this basis, it is to be expected that some concrete mixes exist which are sufficiently rich in cement for aggregate particles still to be held apart even by the dispersed paste after addition of admixture. For these mixes, admixture addition will either leave the plastic viscosity unchanged or decrease it slightly. In fact,



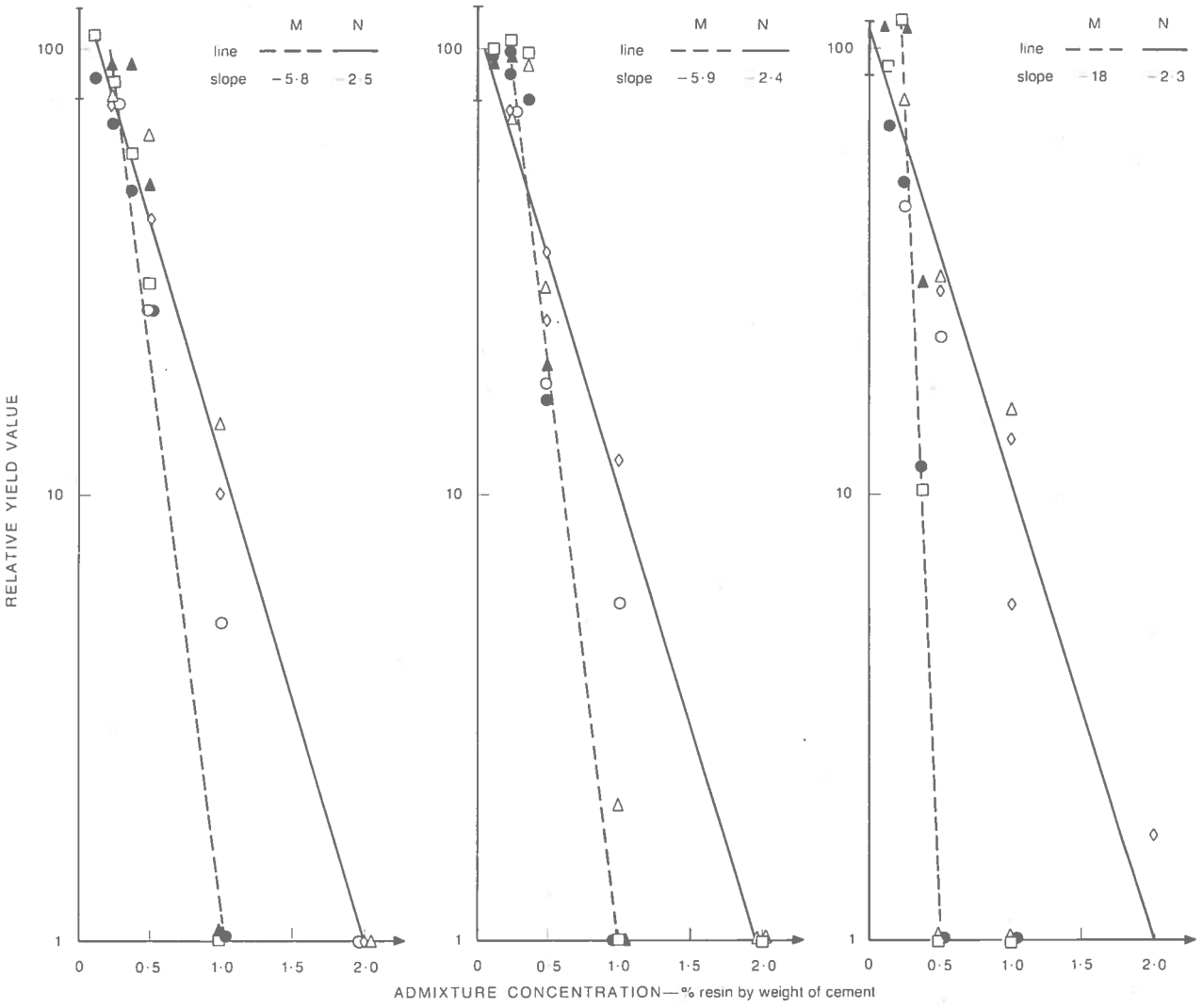
(a) Cement A

Figure 6: Effect of concentration upon yield value.

Tattersall and Dimond in a private communication have reported mixes where it did decrease. The foregoing confirms that concrete rheology and cement paste rheology are very complicated and that extreme caution must be exercised in trying to relate the properties of one to the other.

The differences in detail between the effect of concentration and type of admixture upon different cements will no be examined. Figures 6a to d are graphs of log (relative yield value) of cement pastes against admixture concentration. Results for each geometry are shown and the least-squares regression lines for type M and type N admixture plotted. In every case, the correlation coefficient for the decreasing part of the graph exceeded 0·98. The 90% confidence limits at 0% admixture are also shown.

The best straight lines for type N admixture pass through the origin (yield value = 100 at 0% admixture), whereas those for type M are significantly steeper and pass through a point to the right (100 at



(b) Cement B *(c) Cement C* *(d) Cement D.*

Figure 6 continued

about 0·25% admixture). This could be taken as indicating that a threshold concentration exists for type M, below which there is no effect upon yield value, and above which yield value drops rapidly to zero. This could be attributed to the need to achieve a certain level of surface coverage of cement before the particles are dispersed. This might be true if the concentration coincided with that of a monolayer, but a surface area calculation shows that 0·25% admixture represents about 20 adsorbed layers. An alternative possibility is the orientation of adsorbed resin molecules, but the size and shape of the repeat unit within the type M polymer is little different from that of the type N, so their behaviour would be expected to be similar. There seems to be no simple explanation for the differences.

The effects of concentration, type of admixture and type of cement upon rheological parameters are summarized in Table 4. In pastes, cement D + type M and cement A + type N behave differently from the other combinations; types M and N behave differently in pastes but not in concrete. There appears to be no interaction between cement type and admixture type and the plastic viscosity, except that, of the 14 results where plastic viscosities were greater than the plain pastes, eight are from pastes of cement A. These differences must be attributed to the specific compositions of the cements. Cement A has a high alkali content, whereas cement D is low in tricalcium aluminate, and it appears that type M admixture behaves anomalously with the latter and type N behaves anomalously with the high-alkali cement. On a sample as small as four, no definite conclusions can be drawn, but indications of anomalous behaviour with certain cements have occasionally been reported elsewhere. Banfill found that the yield value and plastic viscosity of concrete increased with time more slowly with the combination of type M and cement D than any of cements A to C[1]. Also, according to a private communication from J. E. Hoult, certain

TABLE 4: **Influence of admixture concentration upon rheology of concrete and of cement paste.**

Property	Type of admixture	Parameter*	Concrete (A, B, C or D)	Paste with cement			
				A	B	C	D
Yield value	M	intercept	0	0·125	0·2	0·25	0·25
		slope	−2·5	−5·3	−5·8	−5·9	−18·4
	N	intercept	0	0	0	0·05	0·05
		slope	−2·1	−1·0	−2·5	−2·4	−2·3
Plastic viscosity	M	intercept	0	0			
		slope	+1·7	−0·7			
	N	intercept	0	0			
		slope	+1·7	−0·2			

*The intercept is the concentration at which the best straight line crosses the lines relative τ_y = 100 and relative μ_p = 1·0, and the slope is the proportionality constant in the relation ln (relative τ_y) ∝ concentration or μ_p ∝ concentration.

sulphonated napthalene formaldehyde resins have behaved anomalously with high-alkali cements, but nothing conclusive has appeared in the literature. Much work needs to be done before these scattered facts can be interpreted and there is no profit in speculating about mechanisms at this stage.

EXPERIMENTAL METHODS

Tables 2 and 3 show that, for plain pastes the down-curves obtained in the three different geometries give different results for yield value and plastic viscosity. Even though the shear cycle is nominally the same in terms of the maximum shear rate and rate of acceleration (Table 1), the yield values are consistently in the order S13/15 < MV11P < H/MVS and the plastic viscosities MV11P ~ S13/15 < H/MVS. However, because the trends with concentration already discussed are reproducible between geometries, this discrepancy is not important in the study of the effect of superplasticizing admixtures, but it is important in the general field of experimental determination of the rheology of cement pastes.

The shape of the flow curves (Figure 3) shows that the cement paste breaks down during the course of the experiment and, because the shear cycles used are similar, it was initially assumed that the degree of structure breakdown is the same for each geometry. This was later found to be untrue. The same pastes were sheared at constant speed in each geometry (the method of reference 20) and the decay of torque with time was monitored with a chart recorder. The torque T dropped from an initial value T_0 to an equilibrium value T_E and the time to reach T_E was much longer for the H/MVS geometry than for the cylinders. At nominally similar shear rates (200 rev/min for MV11P and S13/15 and 1000 rev/min for H/MVS) the degree of breakdown at one minute as measured by the ratio $(T_0 - T)/(T_0 - T_E)$ was 0·97 for MV11P and S13/15 but only 0·80 for H/MVS. The apparent viscosity at the same shear rate after one minute for the H/MVS geometry is roughly twice that for the other two geometries, in accord with the data of Table 2. Thus the discrepancy appears to be due to the fact that the down-curve for cylindrical geometries is measuring an almost fully broken down paste, whereas that for the H/MVS geometry is measuring a partly broken down paste. This also explains the wide scatter of the results shown in Figures 4 and 5, since the degree of breakdown is not necessarily identical in each test.

Further support for this hypothesis is given by attempts to prepare fully broken down pastes for determination in the viscometer. After being mixed by hand, as described already, the paste was mixed for increasing times with a Gallenkamp stirrer at about 2800 rev/min by using the propellor turbine in a 250 ml beaker. The effect of stirring time upon yield value and plastic viscosity is shown in Figure 7. Both parameters have decreased to a constant value by 5 min stirring. Following this procedure, the shear cycles used in the main work were carried out on a 'fully broken down' paste. For cement C at w/c = 0·35, the down-curves give the data of Table 5. This

TABLE 5: **Rheological parameters for 'fully broken down' paste.**

Geometry	Yield value (N/m²)	Plastic viscosity (N s/m²)
MV11P	28·4	0·19
	30·2*	0·23*
S13/15	26·6*	0·23*
	28·7*	0·15*
H/MVS	23·7	0·62
	25·0*	0·47*

*denotes a reversible flow curve, i.e. the up- and down-curves can be superimposed.

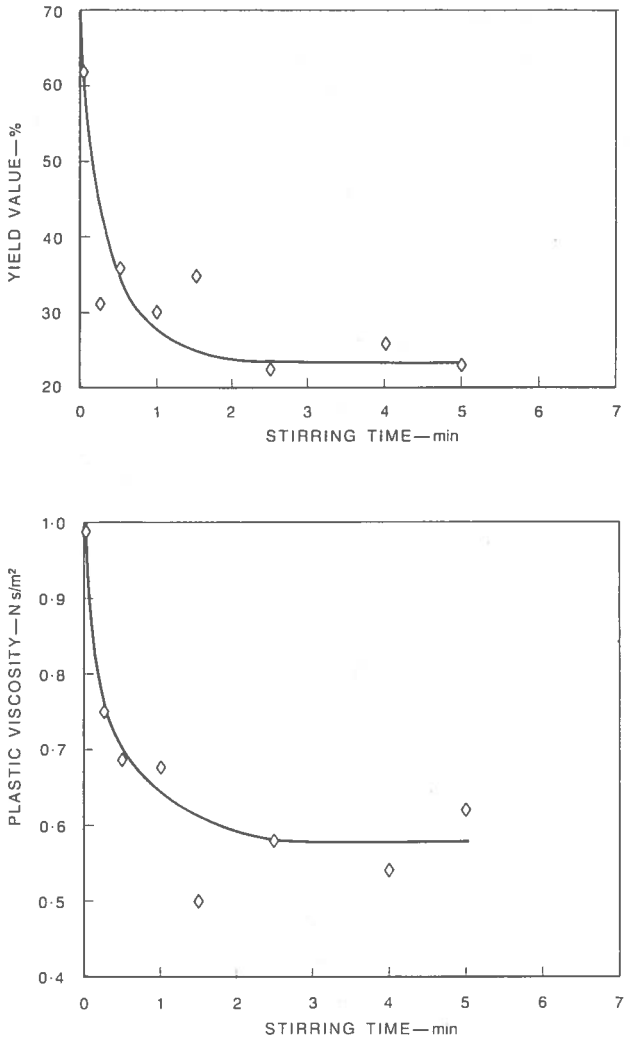


Figure 7: Effect of stirring time upon yield value and plastic viscosity of cement pastes. Cement C, w/c = 0·35, geometry H/MVS, stirrer Gallenkamp SWP-700-P (2800 rev/min).

discrepancy in yield values is completely removed, but there remains a difference between plastic viscosity for the H/MVS geometry and for the other two.

On the assumption that this might have been due to faulty calibration of the viscometer with H/MVS geometry, a 5% solution of Laponite was prepared and its flow curve determined in all three geometries. The behaviour of this material approximates to that of a Bingham. The agreement between geometries was impressive – yield value 60 N/m², plastic viscosity 0·2 N s/m², no geometry deviating by more than 4% from these values. Thus faulty calibration clearly cannot explain the discrepancy in plastic viscosity.

The H/MVS geometry was designed to prevent possible problems with sedimentation during the experiment. If this occurs, changes in the measured flow curves are inevitable. A scaled-up version of this geometry was made which included sampling points at several heights in the outer cylinder. By simply withdrawing a sample with a syringe and evaporating to dryness, the solid concentration of cement in the paste could be determined. This remained constant during shearing of all pastes below w/c = 0·45, i.e. the helical impeller was performing satisfactorily in keeping the solids suspended. Sedimentation in the coaxial-cylinders geometries is also a possibility, and is currently under investigation in the same apparatus.

The remaining consideration is the possible existence of a plug of unsheared material[20]. Visual observation of pastes in the H/MVS geometry is possible during the experiment and flow always took place throughout the material. Critical examination of the paste afterwards showed that it was homogeneous, i.e. plug flow had not occurred. This indicates that the calibration constants for this geometry, which were determined using fluids which do not exhibit plug flow, are likely to be correct.

Visual observation of pastes in cylindrical geometries is not easy because of the construction of the viscometer, but it was considered that plug flow, if present, would be developed by the time the maximum rotational speed was reached. Therefore fully broken down pastes were loaded in the viscometer normally and the shear rate increased at the standard rate (Table 1). At the maximum speed the rotation was stopped abruptly, the viscometer dismantled and the paste examined. With both MV11P and S13/15 geometries there were two distinct zones of paste – one relatively 'runny' which could be poured from the cup, the other relatively solid which stuck to the surface of the outer cylinder. This is clear evidence of plug flow. In this case the down-curve shows the behaviour of the cement paste in the sheared zone only, i.e. the dimensions of the viscometer used in the Reiner–Riwlin equation[24] must be altered to take account of the stationary plug. Crude measurement of the stationary plug indicated that the effective gap width had been reduced to about 1 mm. Applying this correction to a flow curve leaves the yield value unchanged but *reduces* the plastic viscosity, thus making the discrepancy of Table 5 even more marked.

The argument about incomplete structural breakdown could be invoked here, since a narrower gap produces higher shear rates so that more breakdown can be expected during the experiment and this might explain the lower plastic viscosities in cylindrical geometries. The obtaining of reversible flow curves in Table 5 with fully broken down pastes negates this since, even where no further breakdown occurs in the experiment, lower plastic viscosities are obtained in cylindrical geometries. A further possibility is that of centrifugal separation of the paste in an experiment, leaving the sheared zone of lower solids concentration than the plug. This was checked in a simple experiment. Samples of paste from a well defined plug and from the sheared zone were analysed. The

solids contents were 0·754 and 0·751 by weight respectively. This difference is not significant, nor will it change the plastic viscosity by more than 6%, according to vom Berg's data[12]. Thus centrifugal separation cannot account for the differences in measured plastic viscosity.

Formation of a plug is not predicted in these conditions from the theory of a Bingham plastic. The data in Table 5 show that the rotational speed at which the shear stress at the outer cylinder exceeds the yield value of the paste is about 50 rev/min. Therefore, if cement paste is a simple Bingham, the plug should be absent when the cylindrical geometry is examined at 200 rev/min. Clearly the fact that a plug is present suggests that it is formed by a different mechanism. A paste which shows breakdown during the course of a flow curve passes through a sharp peak at low shear rates, e.g. Figure 3, curve I. The yield value calculated from this peak height is about 300 N/m² and plug flow would not be eliminated at a maximum speed of 200 rev/min. Only if plug flow is assumed to occur as a result of the initial yield value at the start of an experiment, rather than the instantaneous yield value during an experiment, can the existence of a plug be explained. But this argument cannot apply to an experiment on a fully broken down paste which has been loaded into the viscometer after shearing (Table 5). The paste never has a yield value high enough to permit plug flow.

Further work

From the experiments described here it is clear that cement paste is a highly intractable material for viscometric study and the following points should be considered in any experimental investigation.

(1) The flow regimes during an experiment should be critically examined for the existence of a plug.
(2) Flow curves should only be used if the cement paste has been fully broken down before the start of the experiment.
(3) More than one geometry should be used in all rheological studies of cement pastes, and only if results agree between geometries should they be accepted.
(4) Use of a helical geometry with smooth cylinders is recommended, as plug flow and sedimentation do not occur.

Outstanding problems which should be resolved are as follows.

(1) The occurrence of plug flow when it is not predicted by the theory of Bingham plastics.
(2) The measurement of different values of plastic viscosity for the same material in different geometries.
(3) The contributions of yield value and plastic viscosity in the structural breakdown of cement pastes.

Conclusions

(1) Superplasticizing admixtures reduce both the yield value and the plastic viscosity of cement paste. They reduce the yield value of fresh concrete, but either reduce or increase the plastic viscosity, depending upon the mix proportions.
(2) The yield value of cement paste is an exponential function of admixture concentration, but sulphonated melamine formaldehyde resin has no effect below 0·2% solids by weight of cement, whereas with sulphonated napthalene formaldehyde resin the effect is immediate.
(3) The sensitivity of the yield value of a cement paste to concentration varies according to the chemical composition of the cement and the type of admixture. These variations are not shown by fresh concrete.
(4) The plastic viscosity of cement paste is more sensitive to melamine than to napthalene type resins. This variation is not shown by fresh concrete.

The results in this paper have been communicated in this relatively inconclusive form with the specific intention of drawing attention to shortcomings in our knowledge and present methods of investigation in this important field, and in the hope that other research workers will be encouraged to start work.

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APPENDIX 1

Properties of the cements

The properties of the cements, which were obtained from the works of Blue Circle Industries Limited, were as follows.

	Cement			
	A (high alkali)	B (low alkali)	C (high C_3A)	D (low C_3A)
COMPOUND COMPOSITION (%)				
C_3S	65·9	59·8	53·7	67·8
C_2S	7·3	8·5	18·2	5·6
C_3A	7·1	8·6	11·6	1·23
C_4AF	10·0	11·2	6·7	15·1
SO_3	2·3	2·5	2·7	2·3
NA_2O	0·36	0·08	0·20	0·24
K_2O	0·87	0·52	0·61	0·36
PHYSICAL PROPERTIES				
Initial set (min)	105	110	170	159
Final set (min)	150	175	215	236
Specific surface (m^2/kg)	344	340	332	385
STRENGTH OF STANDARD CONCRETE (N/mm^2)				
At 3 days	27·0	21·4	22·5	23·7
At 7 days	34·1	29·9	32·4	33·7
At 28 days	43·4	42·2	43·0	40·7

Contributions discussing the above paper should be in the hands of the Editor not later than 30 September 1981.

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The conduction of electricity through concrete

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SYNOPSIS

This paper examines the relationship between mix proportions, electrical properties of the constituents of concrete and the over-all electrical resistivity for concrete. The mechanisms for the conduction of electricity through the heterogeneous medium of concrete are discussed and an electrical model is proposed. Analysis from a purely theoretical standpoint is also described and the values of electrical resistivity obtained experimentally are shown to compare favourably with the theoretical model.

Introduction

Comparatively little work has been undertaken on the electrical properties of cements and even less on concretes, especially on the variation of electrical resistivity during the stages of initial setting and subsequent hardening. The characteristics of cement vary considerably throughout the setting process and, consequently, the relative importance of such factors as polarization and capacitance changes with the age of the concrete. Furthermore, the electrical properties may not be constant throughout the specimen of concrete for the following reasons:

(1) concrete itself is a heterogeneous material;
(2) stratification occurs during placing;
(3) subsequent drying out takes place preferentially from the exposed surfaces, resulting in a moisture gradient from the centre to the exposed face of the concrete.

The present work has been concentrated on the measurement of the electrical properties of concretes of different mixes and water/cement ratios, these mixes being typical of those used in concrete structures. Comparative data on specimens of neat cement pastes and mortars were also obtained. Investigation has been made of the variation of electrical resistivity of concrete during the initial setting period (i.e. the first 24 hours) and throughout the hardening process.

Considerable progress has been made in relating the physical and mechanical properties of concretes (e.g. elastic modulus, shrinkage, creep and Poisson's ratio) to the corresponding properties and volume fractions of the constituent aggregate and hardened cement paste but, as yet, a similar pattern of interrelated behaviour has not been established for electrical resistivity characteristics. In this paper, the experimental data obtained are examined closely in an attempt to assess how the electrical resistivity of cement pastes, mortars and concretes is affected by the mix proportions, water/cement ratio and temperature of the specimens. From this examination, an electrical and theoretical model for the conduction of current is proposed.

Review of previous work

Most of the earlier work in this field[1–4] has been undertaken on cement pastes and directed towards obtaining information about the changes in electrical resistance during the first twenty-four hours of the setting process. The electrical resistivity of air-dried Portland cement paste and concrete has been the subject of investigation by several researchers[5, 6], who concluded that the resistivity of such specimens lies in the region 6·54–11·4 kΩ m and, hence, that the material is a very good insulator.

Hammond and Robson[7] undertook a limited study of the a.c. and d.c. electrical properties of different cements and concretes. They concluded that,

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